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(54) Soil release promoting non-ionic detergent composition

(57) A particulate built nonionic synthetic organic detergent composition, useful for washing synthetic organic polymeric fibrous materials, such as polyesters and polyester-cotton blends and imparting to them soil release properties, while maintaining them comfortable to a wearer and not preventing vapour transmission through them, includes amounts in certain ranges of percentages of nonionic synthetic organic detergent, builder or mixture of builders for such detergent, and a polymer of polyethylene terephthalate and polyoxyethylene terephthalate preferably of a molecular weight in the range of about 15,000 to 50,000. Also disclosed are process for manufacturing such compositions and processes for washing laundry with them.

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The Chemical formulae appearing in the printed specification were submitted after the date of filing, the formulae originally submitted being incapable of being satisfactorily reproduced.

SPECIFICATION

Soil release promoting non-ionic detergent composition

The present invention relates to detergent compositions which are useful for washing synthetic organic polymeric fibrous materials, such as polyesters, and which impart soil releasing properties to such washed materials. More particularly, the invention relates to such compositions which contain a particular type of polymer of polyethylene terephthalate and polyoxyethylene terephthalate which not only imparts soil release characteristics to the washed material but also, unlike some other soil release agents, does not so change the characteristics of the washed material as to make it appreciably less comfortable by preventing or objectionably diminishing vapour transmission through it. The compositions of the present invention also have been found to inhibit redeposition of soil onto the washed material. The invention also relates to processes for making and using the described compositions.

The technical literature includes disclosures of polymeric materials having both hydrophilic and lipophilic properties which can be applied to fibrous substrates to promote soil release therefrom. Such materials are believed to form a coating on the fibres, to which coating the soiling material, such as an oily or greasy substance, does not adhere as strongly as it would to the substrate fibres. Thus, during washing of laundry any soil is more readily removed from materials that have previously been treated with a soil release promoting polymer. Although such a polymer may be applied to a textile material or clothing article when it is being manufactured such an application may be insufficient to keep the item soil releasing during all of its intended life. Also, if a heavy application of the polymer is applied at the time of manufacture it may adversely affect the properties of the fabric, as by making it less capable of moisture transmission and thereby making it less comfortable to a wearer of a clothing item made from such a treated material. Additionally, comparatively heavy applications of the polymer can adversely affect the feel of the fabric.

The problems mentioned above can be avoided by applying smaller proportions of a soil release promoting polymer periodically during the life of a garment or other textile product. One way of accomplishing this is by incorporating such material in a detergent composition with which the item will be washed periodically. Thus, theoretically at least, during washing the polymer will be deposited on the fibrous substrate, where it will remain during rinsing and drying, so that any soiling material that is subsequently deposited on the washed article will be more readily released during the next washing. Although the concept is relatively simple theoretically, as a practical matter it may be very difficult to formulate a detergent composition including a soil release promoting polymer so that the composition will produce the desired effects. Thus, the composition should be compatible with the detergent and builder (and any adjuvants present), should be sufficiently substantive to the textile material so as to be depositable thereon from the dilute washing solution, should not adversely affect the vapour transmission or feel of the textile, should not give the textile an objectionable appearance and should not build up objectionable concentrations on the textile despite repeated washes. A suitable polymer will possess a special balance of properties and so will the detergent composition incorporating it, to make them commercially acceptable. Also, the soil release promoting detergent composition will be of such characteristics that when it is added to the wash water objectionable reactions with the wash water ions and/or with solubilized components of the composition, which could inactivate the polymer, do not occur.

One way of stabilizing the soil release promoting agent so that it does not lose an excessive proportion of its release promoting characteristics on storage is to "insulate" it from materials that tend to react with it. It has been noted that various water soluble salts and builders which are useful in detergent compositions may adversely affect the stabilities in wash water of soil release promoting copolymers of polyethylene terephthalate and polyoxyethylene terephthalate. Such destabilization is of greatest concern when the builder salts or other components of the detergent composition are water soluble and are alkaline in aqueous media. Detrimental hydrolysis or other adverse reactions with the soil release polymer have been noted at pH's of 8 or more, e.g. 9—11, and such degradation or alteration of the polymer so that it loses its desirable soil release promoting characteristics becomes more severe as the pH is increased. In addition, it has been found that the presence of anionic detergent(s) can promote such destabilization. Apparently, any adverse reaction in the wash water between builder salts and the release polymer, when the builder and polymer are in a nonionic detergent composition or are used with such a detergent, either does not occur or does not prevent the polymer from being effective to promote soil release from washed laundry. However, the presence of anionic detergent and/or alkaline builder with the soil release polymer in a liquid product or particulate product containing sufficient moisture to facilitate hydrolysis of the polymer can cause losses in soil release properties during storage, especially if that storage is under high temperature, high humidity conditions. Therefore, it is desirable for detergent compositions containing soil release promoting polymers, such as those mentioned herein, to be non-alkaline, anhydrous (or nearly so) and non-anionic. However, as a practical matter some moisture will normally be present in the detergent compositions and many effective builders for such compositions are alkaline. Thus, for detergent compositions in which alkaline builders are to be employed and which may contain moisture, either

initially, or absorbed during storage, it is important to prevent or sufficiently limit any adverse reaction of soil release promoting polymer with alkaline material.

It has been found that by a method described herein the soil release promoting copolymer may be uniformly distributed throughout the particulate detergent product and such product will be satisfactorily free flowing and uniform in appearance. Also, upon addition of the detergent composition to the wash water it will dissolve readily and the polymer will be quickly and uniformly distributed throughout the wash water. Such method requires little extra equipment, and additional processing time needed is minimal. Also, although the copolymer is homogeneously distributed throughout the detergent composition it is largely insulated from adverse reaction with any alkaline material, especially when moisture contents of the polymer and base beads are lower, and therefore is less subject to hydrolysis or other detrimental reaction which could reduce its soil release promoting activity.

In accordance with a preferred aspect of the present invention a particulate built nonionic synthetic organic detergent composition for washing synthetic organic polymeric fibrous materials especially polyester materials comprises from 5 to 30% of synthetic organic nonionic detergent, 30 to 80% of one or more builders for such detergent, 1 to 20% of water, and a percentage, within the range of 0.5 to 20%, sufficient to impart soil release properties to synthetic organic polymeric fibrous materials especially polyester materials washed with the detergent composition while maintaining them comfortable to a wearer and not preventing vapour transmission through them, of a polymer of polyethylene terephthalate and polyoxyethylene terephthalate of a molecular weight in the range of about 15,000 to 50,000, wherein the polyoxyethylene of the polyoxyethylene terephthalate is of a molecular weight in the range of about 1,000 to 10,000, and the molar ratio of ethylene terephthalate to polyoxyethylene terephthalate units is within the range of 2:1 to 6:1. Preferably, the detergent composition is of a bulk density in the range of 0.4 or 0.5 to 0.9 g/cc, but it can be decreased to as low as 0.2 g/cc. Preferably the nonionic detergent is a condensation product of a higher fatty alcohol of 12 to 16 carbon atoms with 3 to 20 mols of ethylene oxide. Preferably the builder is a water softening zeolite, sodium carbonate, sodium bicarbonate, sodium tripolyphosphate, sodium pyrophosphate, sodium nitrilotriacetate or sodium silicate, or a mixture thereof. Preferably the polymer is of a molecular weight in the range of about 19,000 to 25,000. Preferably the polyoxyethylene of the polyoxyethylene terephthalate is of a molecular weight in the range of 3,000 to 4,000. Preferably the molar ratio of ethylene terephthalate to polyoxyethylene terephthalate units in the polymer is within the range of 3:1 to 4:1. Preferably the molar ratio of ethylene oxide to phthalic moiety in the polyoxyethylene terephthalate is from 20:1 to 30:1. Preferably the percentage of polymer present is in the range of 1 to 10%, more preferably 2 to 5%.

The compositions of the present invention are preferably employed in a washing method according to the invention which comprises washing synthetic organic polymeric fibrous materials in an aqueous medium in a washing machine tube, which medium contains from 0.005 to 0.15% of synthetic organic nonionic detergent, 0.03 to 0.40% of builder for such detergent, and a percentage, within the range of 0.0005 to 0.10%, sufficient to impart soil release properties to the fibrous materials being washed, of a polymer of polyethylene terephthalate and polyoxyethylene terephthalate of a molecular weight in the range of about 15,000 to 50,000, wherein the polyoxyethylene of the polyoxyethylene terephthalate is of a molecular weight in the range of about 1,000 to 10,000, and the molar ratio of polyethylene terephthalate to polyoxyethylene terephthalate units is within the range of 2:1 to 6:1. Preferably such method is carried out by adding a soil release promoting detergent composition of the type hereinabove described to the wash water in a suitable washing machine tub. Also within the invention is a particular built nonionic synthetic organic detergent composition for washing synthetic organic polymeric fibrous materials and imparting soil release properties to them which preferably comprises from 5 to 30% of synthetic organic nonionic detergent, 30 to 80% of builder for such detergent, 1 to 20% of water, and a percentage, within the range 0.5 to 20%, sufficient to impart soil properties to synthetic organic polymeric fibrous materials washed with the detergent composition, of a soil release promoting polymer of polyethylene terephthalate and polyoxyethylene terephthalate, in which detergent composition the nonionic detergent is absorbed into absorbent particles of the builder and the soil release polymer is also post-applied to the said particles.

The described detergent compositions are preferably made by preparing particles of a builder or a mixture of builders for a nonionic detergent, dissolving and/or dispersing in such nonionic detergent in liquid state a substantially anhydrous soil release promoting polymer of polyethylene terephthalate and polyoxyethylene terephthalate and spraying such liquid nonionic detergent-polymer mixture onto moving surfaces of the builder particles to distribute such nonionic detergent and polymer over such particles. Such polymer-nonionic detergent composition is also considered to be an aspect of the present invention.

Although various nonionic detergents of satisfactory physical characteristics may be utilized, including condensation products of ethylene oxide and propylene oxide with each other and with hydroxyl-containing bases, such as nonyl phenol and Oxo-type alcohols, for best results it is highly preferred that the nonionic detergent be a condensation product of ethylene oxide and higher fatty alcohol. In such products the higher fatty alcohol is desirably of 10 to 20 carbon atoms, preferably 12

to 15 or 16 carbon atoms, and the nonionic detergent desirably contains from about 3 to 20 or 30 ethylene oxide groups per mol, preferably from 6 to 11 or 12. Most preferably, the nonionic detergent will be one in which the higher fatty alcohol is of about 12 to 15 or 12 to 14 carbon atoms and which contains from 6 or 7 to 11 mols of ethylene oxide. Among such detergents is Alfonic (Registered Trade Mark) 1214-60C, sold by the Conoco division of E. I. DuPont de Nemours, Inc., and Neodols (Registered Trade Mark) 23-6.5 and 25-7, available from Shell Chemical Company. Among their especially attractive properties, in addition to good detergency with respect to oil and greasy soil deposits on goods to be washed, and excellent compatibility with the polymeric release agents of the present invention, is a comparatively low melting point, often in the range of about 40 or 45 to 65°C, e.g. 45 to 50°C, which is still appreciably above room temperature, so that they may be sprayed onto base beads as a liquid which solidifies quickly after it has penetrated into the beads. Sometimes nonionic detergents of melting points as low as 30°C or 35°C may be used but because such could liquify when the product is used (and stored) in hot climates such detergents may often be avoided.

Various builders and combinations thereof which are effective to complement the washing action of the nonionic synthetic organic detergent(s) and to improve such action include both water soluble and water insoluble builders. Of the water soluble builders, which preferably are employed in admixture, both inorganic and organic builders may be useful. Among the inorganic builders those of preference include various phosphates, preferably polyphosphates, such as the tripolyphosphates and pyrophosphates, more specifically the sodium tripolyphosphate and tetrasodium pyrophosphate; sodium carbonate; sodium bicarbonate; and sodium silicate; and mixtures thereof. Instead of a mixture of sodium carbonate and sodium bicarbonate, sodium sesquicarbonate may often be substituted. The sodium silicate is normally of $Na_2O:SiO_2$ ratio within the range of 1:1.6 to 1:3, preferably 1:2.0 to 1:2.4 or 1:2.8, e.g. 1:2.4. Of the water soluble inorganic builder salts the phosphates will usually be employed with a lesser proportion of sodium silicate, the carbonate will be employed with bicarbonate and often with a lesser proportion of sodium silicate, and the silicate will rarely be used alone. Instead of individual polyphosphates being utilized it will sometimes be preferred to employ mixtures of sodium pyrophosphate and sodium tripolyphosphate in proportions within the range of 1:10 to 10:1, preferably 1:5 to 5:1. Of course, it is recognized that changes in phosphate chemical structure may occur during crutching and spray drying, so that the final product may differ somewhat from the components charged to the crutcher.

Of the water soluble organic builders nitrilotriacetic acid salts, e.g. trisodium nitrilotriacetate (NTA), preferably employed as the monohydrate, are preferred. Other nitriloatriacetates, such as disodium nitrilotriacetate, are also useful. The various water soluble builder salts may be utilized in hydrated forms, which are often preferred. Other water soluble builders that are considered to be effective include the inorganic and organic phosphates, borates, e.g. borax, citrates, gluconates, ethylene diamine tetraacetates and iminodiacetates. Preferably the various builders will be in the form of their alkali metal salts, either the sodium or potassium salts, or mixtures thereof, but sodium salts are normally preferred. In some instances, as when neutral or slightly acidic detergent compositions are being produced, acid forms of the builders, especially of the organic builders, may be preferable but normally the salts will either be neutral or basic in nature, and usually a 1% aqueous solution of the detergent composition will be of a pH in the range of 9 to 11.5, e.g. 9 to 10.5.

Although insoluble builders, generally of the zeolite type, may be used advantageously in the compositions of the present invention, hydrated Zeolite A will be employed most frequently. Nevertheless, Zeolites X and Y may be useful too, as may be naturally occurring zeolites and zeolite-like materials and other ion-exchanging insoluble compounds that can act as detergent builders. Of the various Zeolite A products, Zeolite 4A has been found to be preferred. Such materials are well known in the art and methods for their manufacture need not be described here. Usually such compounds will be of the formula

$$(Na_2O)_x \cdot (Al_2O_3)_y \cdot (SiO_2)_z \cdot w\,H_2O$$

wherein x is 1, y is from 0.8 to 1.2, preferably about 1, z is from 1.5 to 3.5, preferably 2 to 3 or about 2, and w is from 0 to 9, preferably 2.5 to 6.

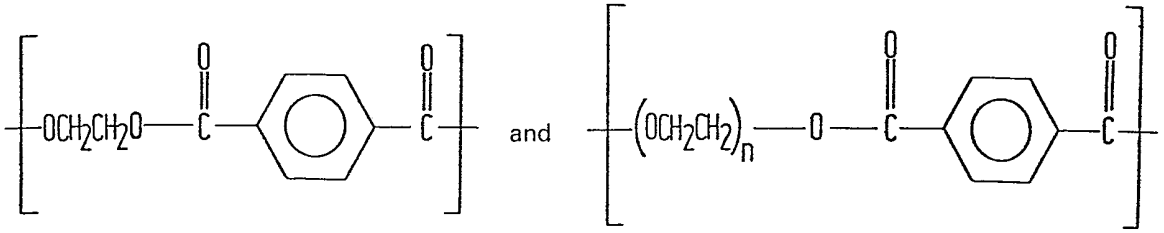
The zeolite builder should be a univalent cation-exchanging zeolite, i.e. it should be an aluminosilicate of a univalent cation such as sodium, potassium, lithium (when practicable) or other alkali metal or ammonium. Preferably the univalent cation of the zeolite molecular sieve is an alkali metal cation, especially sodium or potassium, and most preferably it is sodium. The zeolites, whether crystalline or amorphous, are capable of reacting sufficiently rapidly with calcium ions in hard water so that, alone or in conjunction with other water softening compounds in the detergent composition, they soften the wash water before adverse reactions of such ions with other components of the synthetic organic detergent composition occur. The zeolites employed may be characterised as having a high exchange capacity for calcium ion, which is normally from about 200 to 400 or more milligram equivalents of calcium carbonate hardness per gram of the aluminosilicate, preferably 250 to 350 mg eq/g, on an anhydrous zeolite basis. Also they preferably reduce the hardness quickly in wash water, usually within the first 30 seconds to five minutes after being added to the wash water, and lower the

hardness to less than a milligram of $CaCO_3$ per litre within such time. The hydrated zeolites will normally be of a moisture content in the range of 5 to 30%, preferably about 15 to 25% and more preferably 17 to 22%, e.g. 20%. The zeolites, as charged to a crutcher mix from which base beads may be made, should be in finely divided state, with the ultimate particle diameters being up to 20 microns, e.g. 0.005 to 20 microns, preferably 0.01 to 8 microns mean particle size, e.g. 3 to 7 microns, if crystalline, and 0.01 to 0.1 micron, e.g. 0.01 to 0.05 micron, if amorphous. Although the ultimate particle sizes are much lower, usually the zeolite particles will be of sizes within the range of No. 100 to 400 sieve, U.S. Sieve Series which have openings 149 microns and 37 microns across respectively, preferably No. 140 to 325 sieve, U.S. Sieve Series which have openings 105 microns and 44 microns across respectively, as charged to the crutcher for the manufacture of the base beads. In the base beads the zeolite(s) will often desirably be accompanied by a suitable builder salt or salts, e.g. sodium carbonate, sodium bicarbonate. Sodium silicate may tend to agglomerate with zeolites so the proportion thereof present in zeolite-built base beads may be limited, as to 2 or 3%, or it may be omitted, especially for carbonate-containing formulations, but sometimes as much as 5 to 10% may be present, in NTA-built products.

Although water soluble builders are useful with the soil release promoting polymers in the present detergent compositions adverse interactions between the polymer and water soluble salts in the presence of moisture are possible, especially when the composition is basic in nature, e.g. with a pH above 8. Since moisture is a component of the present detergent composition particles, and its presence does help such particles to be held together better and to be less friable, often it may be preferable to utilize insoluble builders, like the ion exchanging zeolites, which may be less reactive with the polymer and thereby may provide compositions with better soil release promoting powers despite lengthy storage in humid atmospheres. The hydrated zeolites hydrated to less than their full hydrating capacity may be useful in this respect because they tend to absorb excess moisture, which moisture absorption can inhibit adverse reactions of any soluble alkaline salts with the polymer which could happen in the presence of such moisture.

The soil release promoting polymer which is an important component of the compositions of the present invention is a polymer of polyethylene terephthalate and polyoxyethylene terephthalate which is dispersible in water and is depositable from wash water containing nonionic detergent and builder for the nonionic detergent, onto synthetic organic polymeric fibrous materials, especially polyesters and polyester blends, so as to impart soil release properties to them, while maintaining them comfortable to a wearer and not preventing or significantly inhibiting vapour transmission through them. Such polymers have also been found to possess anti-redeposition properties. They tend to maintain soil, such as oily soil, dispersed in wash water during washing and rinsing, so that it is not redeposited on the laundry. Useful such products are copolymers of ethylene glycol or another suitable source of ethylene oxide moiety, such as polyoxyethylene glycol and terephthalic acid or a suitable source of the terephthalic moiety. The copolymers may also be considered to be condensation products of polyethylene terephthalate, which may sometimes be referred to as an ethylene terephthalate polymer, and polyoxyethylene terephthalate. While the terephthalic moiety is preferred as the sole dibasic acid moiety in the polymer it is within the invention to utilize relatively small proportions of isophthalic acid and/or orthophthalic acid (and sometimes other dibasic acids, too) to modify the properties of the polymer. However, the proportions of such acids or sources of such moieties charged to any reaction mix and the corresponding proportions in the final polymer will normally be less than 10% each of the total phthalic moieties present and preferably will be less than 5% thereof.

For best characteristics the molecular weight of the polymer will be in the range of about 15,000 to 50,000, preferably being about 19,000 to 43,000, more preferably being about 19,000 or 20,000 to 25,000, e.g. about 22,000, but sometimes may be as low as 8,000 or as high as 60,000. Such molecular weights are weight average molecular weights, as distinguished from number average molecular weights, which, in the case of the present polymers, are often lower. In the polymers utilized the polyoxyethylene will be of a molecular weight in the range of about 500 or 1,000 to 10,000, preferably about 2,500 to 5,000, more preferably 3,000 to 4,000, e.g. about 3,400. In such polymers the molar ratio of polyethylene terephthalate to polyoxyethylene terephthalate units (considering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as such units) will be within the range of 2:1 to 6:1, highly preferably 5:2 to 5:1, even more preferably 3:1 to 4:1, e.g. about 3:1. The proportion of ethylene oxide to phthalic moiety in the polymer will be at least 10:1 and often will be 20:1 or more, preferably being within the range of 20:1 to 30:1 and more preferably being about 22:1. Thus, it is seen that the polymer may be considered as being essentially a modified ethylene oxide polymer with the phthalic moiety being only a minor component thereof, whether calculated on a molar or weight basis. It is considered surprising that with such a small proportion of ethylene terephthalate or polyethylene terephthalate in the polymer the polymer is sufficiently similar to the polymer of the polyester fibre substrate (or other polymers to which it is adherent, such as polyamides) as to be retained thereon during the washing, rinsing and drying operations. Yet, as shown by comparative experiments and various washing tests, in which soil release is measured, the described polymer, in the present detergent compositions, is effective to deposit on washed synthetics, especially polyesters, and to make them better able to be washed free of oily soil by a built nonionic detergent composition. It is considered that its increased hydrophilicity, attributable to the large proportion of hydrophilic ethylene oxide moieties therein, may be responsible for the excellent soil release properties which it imparts to the material upon which it is deposited, and such may also help it to coact with the built nonionic detergent.

Although suitable methods for making the polymers of the present invention are described in the literature it is considered that none of them discloses the particular described polymers and none disclose the present detergent compositions. Such polymers may be considered as having been randomly constructed from polyethylene terephthalate and polyoxyethylene terephthalate moieties, such as may be obtained by reacting polyethylene terephthalate (e.g. spinning grade) and polyoxyethylene terephthalate or reacting the ethylene and polyoxyethylene glycols and acid (or methyl ester) precursors thereof. Yet, it is also within the present invention to utilize more ordered copolymers, such as those made by reacting components of predetermined or known chain lengths or molecular weights, so as to produce what might be referred to as block copolymers or non-random copolymers. Graft polymers may also be practicable. Also, the described processes of making useful soil release promoting detergent compositions are also practicable with other polyethylene terephthalate-polyoxyethylene terephthalate copolymers, and the nonionic detergent-polymer solutions or dispersions can be made from such other polymers.

The described materials are available from various sources, the products of one of which will be described in more detail here. Useful copolymers for the manufacture of the detergent compositions of the present invention are marketed by Alkaril Chemicals, Inc. and commercial products of such company that have been successfully employed to produce satisfactory soil release promoting detergent compositions are those sold by them under the trademarks Alkaril QCJ and Alkaril QCF, formerly Quaker QCJ and Quaker QCF. Products available from them in limited quantities, designated by them as 2056-34B and 2056-41, have also been found to be acceptable. The QCJ product, normally supplied as an aqueous dispersion, is also available as an essentially dry solid. When it is anhydrous or low in moisture content (preferably less than 2% moisture), it looks like a light brown wax in which the molar ratio of ethylene oxide to phthalic moiety is about 22:1. In a 16% dispersion the viscosity at 100°F (38°C), is about 96 centistokes. The 2056-41 polymer is like a hard, light brown wax and in it the hydrophile:hydrophobe ratio is about 16 to 1, with the viscosity being about 265 centistokes. The 2056-34B polymer appears to be a hard brown wax, with a hydrophile:hydrophobe ratio of about 10.9:1 and its viscosity, under the same conditions as previously mentioned, is about 255. Thus, the higher the molecular weight of the polymer the lower the hydrophile:hydrophobe molar ratio may be therein and still result in satisfactory soil release promotion by the detergent compositions of the present invention. The QCJ and QCF polymers have melting points (by differential thermal analysis) of about 50 to 60°C, a carboxyl analysis of 5 to 30 equivalents/10^6 grams and a pH of 6 to 8 in distilled water at 5% concentration. The molecular weights (weight average) are in the range of 20,000 to 25,000 and the ethylene terephthalate:polyoxyethylene terephthalate units molar ratio is about 74:26. All three of the above-mentioned trademarked products are water soluble in warm or hot water (at 40 to 70°C) or at least are readily dispersible, and may be characterised as of high molecular weight, over 15,000, generally in the range of 19,000 to 43,000, often preferably 20,000 to 25,000, e.g. about 22,000. Normally, for "solution" application to materials or for solution addition to a detergent composition in wash water, the copolymers of the present invention may be employed in aqueous dispersion. In such dispersions a surface active agent may be present to assist in maintaining the dispersion uniform. Only small proportions of such surface active agent will be employed, if any, and among those that have been found to be useful are the quaternary ammonium halides and other suitable cationic surface active agents. Normally, the concentration of the polymer in the aqueous medium will be about 5 to 25%, on a composition basis, preferably 10 to 20%, e.g. 16%, and such is the concentration at which the mentioned commercial products are normally supplied when a liquid form is desired. Generally, the proportion of cationic surface active agent present, if any at all, will be from 0.5 to 5%, preferably 1 to 3%, e.g. 2%, in the liquid preparation, or 3 to 30%, preferably 5 to 20%, e.g. 13% with the solid polymer. While liquid dispersions or solvent solutions of the polymer may be employed for direct additions of the polymer to the medium in which the fabrics are to be treated, when the polymer is to be incorporated in a particulate detergent composition it will be preferable for it

to be in solid form, preferably as a particulate solid of a particle size like that of the other detergent composition components. Alternatively, it may be finely divided and powdered onto spray dried beads of the other components. In more preferred methods of incorporation in a detergent composition the polymer may be dissolved in nonionic detergent, preferably essentially anhydrous, and sprayed onto base beads, but it may also be prilled with carriers and mixed with the base beads. It has been found that the polymer should not be added to an aqueous crutcher mix containing anionic detergent and/or builder salt and it should not be brought into contact with water soluble builder salt in the presence of moisture, especially at an elevated temperature. Accordingly, to make free flowing particulate product, normally, the polymer will be essentially dry or very low in moisture content. The use of such a product also allows for the manufacture of base beads at normal moisture content without the moisture content thereof being increased objectionably by post-spraying of an aqueous dispersion of the polymer onto the beads.

Various suitable adjuvants may be present in the detergent compositions of the present invention, such as bentonite, which contributes softening properties to the product and helps cause the product to disperse rapidly in wash water; polyacrylate which desirably promotes dispersion of the product and provides bead strength and bulk density and porosity control (and also, like the bentonite, helps to promote spray drying and improve drying efficiency); enzyme powder which helps to decompose stains and other soils so as to promote their removal, thereby coacting with the soil release promoting polymer; perfumes; fluorescent brighteners; bleaches, e.g. sodium perborate; colourants (dyes and water dispersible pigments, such as ultramarine blue); bactericides; fungicides; and flow promoting agents; some of which materials may be added in the crutcher so that they are parts of the base beads, and some of which may be post-added. Inorganic fillers, such as sodium sulphate and sodium chloride, may be utilized but preferably the proportions thereof will be limited because it has been found that sodium sulphate tends to react adversely with the present polymers. Of the enzymes, both proteolytic and amylolytic enzymes may be employed, such as those sold under the tradenames Alcalase, manufactured by Novo Industri, A/S, and Maxazyme, both of which are alkaline proteases (subtilisin).

In the detergent compositions of the present invention the proportion of synthetic organic nonionic detergent will be from 5 to 30%, preferably 10 to 25% and more preferably 18 to 22%, e.g. about 20%. The proportion of builder will be from 30 to 80%, preferably from 40 to 80%, more preferably 50 to 75%. The proportion of soil release promoting polymer will be from 0.5 to 20%, preferably 1 to 10%, more preferably 1 to 5% and most preferably 2 to 5%, e.g. 3%. The moisture content of the product will be from 1 to 20%, preferably 2 to 15% and more preferably 2 to 10 or 12%. The moisture content may be higher with compositions in which the builder is a partially hydrated zeolite and which do not contain sodium sulphate. Individual adjuvants are preferably no more than 10% of the composition, more preferably being limited to 5% and often to 2 or 3%, with the total of adjuvants desirably not exceeding 25%, preferably being limited to 15% and more preferably being held to 5 to 10% of the composition (except when bentonite is one of such adjuvants, in which case the proportion thereof may be increased by up to 5 or 10%).

When bentonite is present it will preferably be a swelling bentonite of the Wyoming type, such as that which has been sold under the trademark THIXO-JEL No. 1 (now Mineral Colloid 101), normally with a swelling capacity in water in the range of 3 to 15 ml/g, preferably 7 to 15 ml/g, and with a viscosity in water in the range of 3 to 30 centipoises, preferably 8 to 30 centipoises at a 6% concentration. The proportion of bentonite, when it is present in the detergent composition, will usually be in the range of 2 to 10%, preferably 4 to 10%. Sodium polyacrylate or other suitably water soluble polyacrylate, when present, will normally be at a concentration within the range of 0.1 to 1%, preferably 0.1 to 0.5%. Enzyme powder, when present, will usually be at a concentration in the range of 0.5 to 3%, preferably 1 to 2%. Such enzyme powder is commercially available as a mixture of active enzyme and carrier material, e.g. Maxazyme 375.

For these detergent compositions wherein zeolite is present with sodium carbonate and sodium bicarbonate, the percentages thereof will usually be within the range of 20 to 35%, 5 to 15% and 15 to 30%, respectively, preferably 25 to 30%, 9 to 14% and 20 to 25%. In such compositions silicate will preferably be avoided or limited to about 2 or 3% of the product, and the moisture content will usually be in the range of 4 to 12%, preferably 6 to 10%. Enzyme, bentonite and sodium polyacrylate will preferably also be present in such products and sometimes more silicate can also be tolerated, as in NTA-built products. For compositions built with carbonate, bicarbonate and sodium silicate, the proportions will usually be 15 to 35%, 20 to 40% and 3 to 15%, respectively, preferably 20 to 30%, 30 to 35% and 8 to 13%, respectively. Enzyme powder will normally also be present and the moisture content will normally be in the range of 2 to 10%, such as 2 to 6%. Other preferred compositions based on combinations of zeolite, NTA, sodium silicate and sodium carbonate will include 20 to 35%, 15 to 40%, 2 to 10%, and 1 to 10% of such materials, respectively, preferably 20 to 30%, 25 to 35%, 3 to 8% and 2 to 5%, respectively. Such products will also desirably contain enzyme, and their moisture contents will usually be in the range of 4 to 12%, preferably 3 to 8%. For phosphate formulas, those wherein the builder is sodium polyphosphate, such as sodium tripolyphosphate, with silicate, the

proportions of such materials will normally be in the ranges of 40 to 75% and 5 to 15%, respectively, preferably 50 to 70% and 6 to 12%, with the moisture content thereof being from 4 to 12%, preferably from 6 to 10%. Such compositions will also preferably contain an enzyme powder. The compositions described will usually also contain a fluorescent brightener, such as that sold under the trademark Tinopal 5BM, a perfume, and optionally, a colouring agent, such as ultramarine blue, Polar Brilliant Blue or Blue Dye No. 5. When setting in the crutcher is a possibility, due to the nature of the crutcher mix, such as one containing carbonate, bicarbonate and silicate-built base beads, anti-gelling or anti-setting agents, such as mixtures of magnesium sulphate and sodium citrate, may be employed and such will then be present in the end product.

The detergent compositions, whether previously manufactured and stored before use, or made immediately prior to use, may be employed in dilute aqueous solution (or dispersion) in wash water to wash all-synthetic materials, including polyester; cotton-synthetic blends, including cotton-polyester blends, cottons; nylons; and mixtures of such materials. Normally the weight ratio of the dry weight of materials being washed to aqueous washing medium will be in the range of 1:20 to 1:5, preferably 1:20 to 1:9, the wash will be conducted with agitation over a period from 5 minutes to 1/2 hour or one hour, often from 10 to 20 minutes, and after washing the materials will be rinsed, usually with several rinses, and will be dried, as in an automatic laundry dryer. The wash water will usually be at a temperature of 10 to 60°C, preferably 20 to 50°C and more preferably 40 to 50°C, and the concentration of the detergent composition or the equivalent components (if separately added to the wash water) will be from 0.05 to 1%, preferably from 0.05 to 0.15%, e.g. 0.06% or 0.13%. More preferred detergent compositions have a bulk density in the range of 0.6 to 0.9 g/cc and such detergents are normally employed at a concentration of about 1/4 cup (or about 40 grams) per wash, with the wash tub usually containing about 17 gallons (U.S.) (litres) of water for top loading machines and about 7 to 8 gallons (to litres) for front loaders. When a "European" type of washing machine is employed, wherein higher concentrations of detergent compositions are utilized, with lesser amounts of water, and normally higher washing temperatures are used, it may be preferable to lower the washing temperatures for best deposition of the polymer on the washed materials. The upper parts of the ranges of detergent composition concentrations previously given may be considered as appropriate for European washing conditions whereas the corresponding lower parts of such ranges are for "American" type top loading washer apparatuses and conditions, with the American front loader concentrations being somewhat intermediate.

The proportions of the individual active components of the present compositions in the wash water will normally be from 0.005 to 0.15% of synthetic organic nonionic detergent, 0.03 to 0.4% of builder for such detergent and 0.0005 to 0.10% of polyethylene terephthalate-polyoxyethylene terephthalate copolymer. Preferably such proportions will be 0.005 to 0.06%, 0.03 to 0.16% and 0.0005 to 0.04%, respectively, and more preferably 0.01 to 0.05%, 0.03 to 0.14% and 0.0005 to 0.02%, respectively. Most preferably the percentage of the polymer present will be in the range of 0.001% to 0.01%, e.g. 0.002%. While such ranges apply to both horizontal and vertical tub machines the horizontal tub sometimes requires lesser proportions of the composition per unit weight of laundry for equal cleaning power. For soil release however, it is advisable to employ concentrations within the ranges given, and to use the amounts of polymer mentioned, although when extra polymer is present less detergent composition may be used.

The base beads which may be employed in making the compositions of the invention are preferably spray dried from an aqueous crutcher mix which normally will contain from about 40 to about 70 or 75% of solids, preferably 50 to 65% thereof, with the balance being water, preferably deionized water, as previously described (but city water may also be employed). The crutcher mix is preferably made by sequentially adding various components thereof in a manner which will result in the most miscible, readily pumpable and non-setting slurry for spray drying. The order of addition of the materials may be varied, depending on the circumstances, but it is highly desirable when "settable" crutcher mixes are employed to add the silicate solution (if any) last, and if not last, at least after the addition of any gel- or "freeze"-preventing combination of materials or processing aids, such as citric acid and magnesium sulphate. Normally it is preferable for all or almost all of the water to be added to the crutcher first, preferably at about the processing temperature, after which the processing aids (if present) and other minor components, including pigment, fluorescent brightener and polyacrylate, if present, are added, followed by most of the builder(s), bentonite and silicate builder (if present). Usually during such additions each component will be mixed in thoroughly before addition of the next component but methods of addition may be varied, depending on the circumstances, so as to allow co-additions when such are feasible. Sometimes component additions may be in two or more parts and sometimes different components may be pre-mixed before addition to speed the mixing process. Normally, mixing speed and power will be increased as the materials are added. For example, low speed may be used until after admixing in of the last of the zeolite or soluble builder, after which the speed may be increased to medium and then to high, at which it will preferably be before, during and after addition of any silicate solution.

The temperature of the aqueous medium in the crutcher will usually be about room temperature or elevated, normally being in the 20 to 80°C range, preferably from 30 to 75 or 80°C, and more

preferably 40 to 70 or 80°C. Heating the crutcher medium may promote solution of the water soluble salts of the mix and thereby increase miscibility but the heating operation, when effected in the crutcher, can slow production rates. Therefore, an advantage of having processing aiding materials present in the mix (especially if any soluble silicate is present), is that they ensure that at lower temperatures non-gelling slurries will result. Temperatures higher than 80°C (and sometimes those higher than 70°C) will usually be avoided because of the possibility of decomposition of one or more of the crutcher mix components, e.g. sodium bicarbonate. Also, in some cases lower crutcher temperatures increase the upper limits of crutcher solids contents, probably due to insolubilizing of normally gelling or setting components.

Crutcher mixing times to obtain good slurries can vary widely, from as little as five minutes in small crutchers and for slurries of higher moisture contents, to as much as four hours, in some cases. The mixing times needed to bring all the crutcher mix components substantially homogeneously together in one medium may be as little as ten minutes but in some cases can take up to an hour, although 30 minutes is a preferable upper limit. Counting any such initial admixing times, normally crutchering periods will be from 15 minutes to two hours, e.g. 20 minutes to one hour, but for the crutcher mix should be such as to be mobile, not gelled or set, for at least one hour, preferably for two hours, and more preferably for four hours or longer after completion of the making of the mix, and preferably will be mobile for as long as 10 to 30 hours to allow for situations wherein other manufacturing problems may be encountered, causing processing delays.

The crutched slurry, with the various salts and other components thereof dissolved or in particulate form and uniformly distributed therein, is transferred in usual manner to a spray drying tower, which is normally located near the crutcher. The slurry is dropped from the bottom of the crutcher to a positive displacement pump, which forces it at high pressure through spray nozzles at the top of a conventional spray tower (countercurrent or concurrent) wherein the droplets of the slurry fall through a hot drying gas, usually the combustion products of fuel oil or natural gas, in which the droplets are dried to desired bead form. During the drying, part of the bicarbonate (if present) may be converted to carbonate, with the release of carbon dioxide, which, in conjunction with the small contents of polyacrylate (if present) in the mix being spray dried, improves the physical characteristics of the beads made, and helps them become more absorptive of liquids, such as liquid nonionic detergent, which may be post-sprayed onto them subsequently. However, the zeolite, bentonite and polyphosphate (when present) components of the base beads made also appear to favour absorption of liquid and the production of a strong bead, and the polyacrylate improves bead characteristics and promotes faster drying, thereby increasing tower throughput.

After drying the product is screened to desired size, e.g. 10 to 60 or 100, U.S. Sieve Series which have openings 2000 microns, 250 microns and 149 microns across respectively, and is ready for application of nonionic detergent spray thereto. Although the foregoing description is of the making of spray dried base beads, and such are preferred for various reasons already mentioned, such as bulk density, uniformity, flowability, strength and sorption properties, it is within the invention to employ other equivalent or nearly equivalent base beads, such as those which are agglomerates, mixtures, granulates, ground beads, prills or chopped filaments. The nonionic detergent will usually be at an elevated temperature, such as 30 to 60°C, e.g. 50°C, to assure that it will be liquid; yet, upon cooling to room temperature it will desirably be solid, often resembling a waxy solid. Even if at room temperature the nonionic detergent is somewhat tacky, this characteristic does not make the final composition poorly flowing because the detergent penetrates to below (or within) the bead surface. The detergent also acts to cover the builder and any other components of the base bead and thus protects any post-applied polyester from contact and reaction with the base bead which might otherwise occur, especially when the builder is alkaline and water soluble, and the composition is stored under a humid atmosphere. Incidentally, the presence of only partially hydrated zeolite in the compositions can lower the relative humidity in sealed containers of the detergent, thereby also aiding in inhibiting hydrolysis of the polyester. The nonionic detergent, applied to moving or tumbling beads as a spray or as droplets, is preferably a condensation product of ethylene oxide and higher fatty alcohol, such as was previously described, but other nonionics may also be operative. The enzyme preparation (herein referred to as enzyme, although it is recognized that it includes a carrier material, too), hydrous silicate, if employed, soil releasing polymer, and any other powdered adjuvants may be dusted onto or mixed with the builder base particles, and perfume and any other liquids to be post-added may be sprayed on at a suitable point before or after addition(s) of the powder(s). When soil release promoting polymer is applied in or with nonionic detergent it is preferred that the base beads, as well as the polymer-detergent, be at an elevated temperature, e.g. 50 to 60°C, so that penetration of the mixture into the base beads may be promoted and so that stable free flowing products will be obtained. The nonionic detergent, by enveloping the polymer, or at least, by diluting it may act to limit contact thereof with the builder salt, thereby stabilizing the polymer and improving soil release by it. Although bentonite may be crutched with the other components of the crutcher mix, and such procedure is preferred, instead (or also) it may be post-added to the base beads or to the base beads with detergent already absorbed therein, either as a powder or as an agglomerate, and if it is added with the polymer it can help to limit contact of the polymer with the builder, and can thereby help to

stabilize the composition. Similar effects can be obtained by pre-mixing the polymer, in powdered or other suitable form, with other chemically non-reactive materials.

The preferred method of applying the polymer and nonionic detergent to base beads includes preparing particles of a builder or a mixture of builders for a nonionic detergent, dissolving and/or dispersing in such nonionic detergent in liquid state a substantially anhydrous soil release promoting polymer and spraying such liquid nonionic detergent-polymer mixture onto moving surfaces of the builder particles to distribute such nonionic detergent and polymer over such particles. More preferably, the soil release promoting polymer is like the preferred ones previously described, the nonionic detergent is a condensation product of a higher fatty alcohol of 12 to 16 carbon atoms with 3 to 20 mols of ethylene oxide per mol of higher fatty alcohol, the builder base beads onto which the nonionic detergent-polymer solution is sprayed include from 60 to 99% of builder and 1 to 20% moisture, and the final detergent composition made includes from 5 to 30% of nonionic synthetic organic detergent, 30 to 80% of builder or mixture of builders in such detergent, 1 to 20% of water and 0.5 to 20% of soil release promoting polymer.

The nonionic detergent-polymer solutions and/or dispersions, suitable for spraying onto detergent builder particles to produce a soil release promoting particulate built nonionic synthetic organic detergent composition, comprise nonionic detergent, in liquid state, having dissolved or suspended therein a soil release promoting polymer. Preferably, the nonionic detergent and soil release promoting polymer are those mentioned herein, the polymer solution produced is of a moisture content less than 2% and the solution is at a temperature in the range of 40 to 70°C, preferably 45 or 50 to 55 or 60°C, at which temperature it is desirably sprayed onto the builder base beads to form a soil release promoting detergent composition.

The liquid nonionic detergent-soil releasing polymer composition, suitable for spraying onto detergent builder base beads or other such particles to make a soil release promoting particulate built nonionic synthetic organic detergent composition, comprises at least a copolymer of polyethylene terephthalate and polyoxyethylene terephthalate and a normally solid condensation product of higher fatty alcohol and ethylene oxide or ethylene glycol, both of which will be anhydrous or of very limited moisture contents, so that the stability of the polymer will be sufficiently maintained on reasonable storage that the detergent composition will have acceptable soil release promoting properties. Generally the moisture contents of the nonionic detergent and the polymer will be no greater than 5% each, preferably no more than 2% each, more preferably up to 0.5% each, most preferably up to 0.2% each, and ideally, each will be completely anhydrous. Correspondingly, such moisture content limits, including a very highly preferred 0.1%, also apply to the spray composition. Although the nonionic detergent is normally solid, some normally liquid detergent, e.g. 5 to 10% or so, may sometimes be incorporated with it, depending on the circumstances, including the flowability of the final detergent composition, and sometimes a normally liquid detergent can be used alone, although this is not preferred.

The concentration of the polymer in the nonionic detergent will normally be in the range of 5 to 30%, preferably 5 to 20% and more preferably 10 to 15%, e.g. about 13%. When other materials are also present in the nonionic detergent with the polymer such percentages will be adjusted accordingly. The amounts of such additional materials, such as colourants, perfume, filler, or dispersing agent, e.g. bentonite, if present, will be limited, with the total thereof rarely exceeding 10%, preferably being limited to 5% and more preferably being no more than 2%. Often any insoluble materials, such as bentonite, will be omitted from the spray, despite some beneficial effects thereof, because they can to some extent inhibit penetration of the liquid material(s) into the particle or base bead interiors, thereby sometimes causing the final composition to be poorly flowing and somewhat tacky.

Spraying of the liquid solution or mixture at elevated temperature onto the base beads may be effected in any of various types of mixing apparatuses, of which tumbling drums are often preferred. Such tumbling drums may be elongated hollow drums, sometimes equipped with baffles or flights to assist in forming curtains of moving base bead particles as the drum rotates. Such drums may be inclined at a suitable angle, usually from 2 to 15° to the horizontal, such as 5 to 10°, and may rotate at a suitable speed, such as from 2 to 30 revolutions per minute, usually 4 to 20 r.p.m. The tumbling time in the drum may be from about 1 to 20 minutes, preferably 2 to 15 minutes and often around 4 to 6 minutes will be sufficient. The liquid droplets of spray may be produced using any standard spray nozzles, and plural nozzles may also be employed. In some cases separate nozzles may be used for perfume and for the detergent-polymer solution. The liquid droplets of the sprays will normally be in the 50 to 500 micron diameter range, preferably 50 to 250 microns, but coarser particles may also be employed providing that absorption is satisfactory and lumping or agglomeration is avoided. Preferably, to avoid such lumping the liquid spray will be directed horizontally or somewhat upwardly onto continuously moving surfaces of the base beads being tumbled in the inclined drum, as they form a "curtain" of particles.

Although a tumbling drum of the type described may be the preferred apparatus for applying the present liquid composition to base beads, it is contemplated that other such apparatuses and mixers may also be employed and although spraying of the liquid onto a curtain of falling (or rising) beads is preferred, other applications of liquid to the base beads, either as droplets, streams, films or in other

forms, may also be satisfactory in particular circumstances. While continuous processes for applying the liquid to the base beads are preferred, batch processes may also be used and often, especially for relatively low production rates, may be more economical and may produce more uniform products.

The invention may be put into practice in various ways and a number of specific embodiments will be described to illustrate the invention with reference to the following examples.

Unless otherwise indicated, all parts are by weight and all temperatures are in °C.

Examples 1 to 4

The compositions of these examples are set out in Table 1A and 1B below, parts being by weight.

Table 1A

No.	*Ingredient*	*Example* 1	2	3	4
1	Nonionic Detergent (Alfonic 1214-60C, 40% C_{12-14} fatty alcohol with 60% of ethylene oxide)	20.0	20.0	20.0	20.0
2	Pentasodium tripolyphosphate	57.0	—	—	—
3	Sodium silicate ($Na_2O:SiO_2$=1:2.4)	9.2	—	5.0	10.8
4	Fluorescent brightener (Tinopal 5BM)	1.3	1.7	1.7	1.7
5	Perfume (Balirose)	0.25	0.25	0.25	0.25
6	Moisture (release after 1/2 hour at 105°C)	7.5	8.0	5.5	2.5
7	Enzyme powder (Alcalase or Maxazyme 375)	1.3	1.3	1.3	1.5
8	Dye (Blue, Mix No. 5)	0.05	—	—	—
9	Dye (Polar Brilliant Blue)	0.44	—	—	—
10	Pigment (ultramarine blue)	—	0.2	0.2	0.2
11	Soil release promoting polymer (QCF or QCJ)	3.0	3.0	3.0	3.0

Table 1B

No.	*Ingredient*	*Example* 1	2	3	4
12	Zeolite Partially hydrated crystalline Zeolite 4A (20% moisture)	—	27.0	24.0	—
13	Bentonite (THIXO-JEL No. 1)	—	5.0	5.0	—
14	Soda Ash	—	11.3	3.0	24.0
15	Sodium bicarbonate	—	22.6	—	33.0
16	Sodium polyacrylate (Alcosperse 107D)	—	0.5	—	—
17	Trisodium nitrilotriacetate monohydrate	—	—	30.0	—
18	Epsom salt	—	—	—	1.0
19	Sodium citrate	—	—	—	0.5

In each of the above compositions the base beads are made by mixing together ingredients 2 to 4, 8 to 10 and 12 to 19 in an aqueous medium in a detergent crutcher, such mix being of all the base components at a 55% solids concentration in deionized water at a temperature of about 60 to 70°C, but lower temperatures may be used for certain formulations. Ingredient 6, the water content, is that of the eventual base beads. During mixing of the various components the mixer speed is increased to medium and ultimately to high and after addition of all the constituents, which takes approximately fifteen minutes, mixing is continued for about an hour (in some cases as much as four hours of mixing may occur), during which time some of the water present, e.g. about 2 to 6%, may be lost by evaporation, and may be replenished, if desired. During the mixing time the crutcher slurry is continuously mobile and does not gel, set or cake. Because bicarbonate partially decomposes to carbonate during spray drying, amounts of bicarbonate and carbonate in the crutcher formulations may be varied, depending on the spray tower operating characteristics.

Starting about five minutes after all the components of the crutcher mix are present, the mix is dropped from the crutcher to a pump, which pumps it at a pressure of about 21 kg/sq cm into the top of a countercurrent spray tower wherein the initial drying air temperature is about 430°C and the final temperature is about 105°C. The base beads resulting are of a bulk density of about 0.4 g/cc for the first formula and about 0.7 g/cc for each of the other formulas after being screened to a particle sizes range substantially between No. 10 and No. 60 sieve, U.S. Sieve Series (which have openings 2000 microns and 250 microns across). Moisture contents thereof are about 9.4%, 10%, 6.9% and 3.1%, respectively. The base beads are free flowing (generally with about an 80% flow index), non-tacky, satisfactorily porous, yet firm on the surfaces thereof and capable of readily absorbing significant proportions of liquid nonionic detergent without becoming objectionably tacky.

The flow index of the product is determined by the following flow test. In this flow test the volumetric flow rates of base beads (and in some cases final product) and standardized Ottawa sand

(—20 +60, U.S. Sieve Series sieve) are compared by measuring the times required for complete emptying of a 1.9 litre Mason jar through a 2.2 cm diameter hole in a nozzle attached to the cap thereof. The flow index is the time for the sand flow divided by the time for the test product flow, expressed as a percentage.

Detergent products are made from the spray dried base beads by spraying the normally waxy nonionic detergent onto the tumbling bead surfaces, preferably while the beads are being mixed in a tumbling drum. Instead of Alfonic 1214-60C, Neodol 23-6.5, 23-7, or 25-7, and sometimes 45-11 may be substituted. The nonionic detergent employed is in heated liquid state, at a temperature of about 45—55°C and the quantity sprayed is such as to result in the final product containing about 20% of nonionic detergent. In some instances, as previously mentioned, the soil release promoting polymer may be dissolved in the nonionic detergent, in which case the temperature of the nonionic detergent and the polymer will ordinarily be in the 45 to 60°C range, preferably at 50—55°C or another suitable temperature at which the polymer is soluble in the nonionic detergent. The proteolytic enzyme is applied in powdered form to result in the desired concentration in the product, and perfume is sprayed onto the product to the extent of its desired concentration therein. The resulting detergent compositions are of bulk densities about the same as or up to 0.1 g/ml higher than those of base beads, but are within the ranges previously recited. The products are attractive and regular in appearance, and are free flowing and non-dusting. Similar products may be made by blending the powdered or particulate soil release promoting polymer of a low moisture content, preferably less than 2%, with the enzyme or with some or all of formula amounts of bentonite, and dusting the mix onto the base beads or blending it with such beads, either before or after application of the nonionic detergent (preferably after). Such applications of the polymer may also be made separately from the enzyme and/or bentonite.

The detergent compositions described above are excellent heavy duty laundry detergents and are especially useful for washing household laundry in automatic washing machines. When employed at a concentration of about 0.05 to 0.15%, e.g. 0.06% in a top loading 17 U.S. gallon (litres) capacity washer, in the washing of normal loads of 100% polyester and 65% polyester — 35% cotton fabrics in home laundry or commercial washing machines, whether of the top loading or front loading types, or at higher concentrations in European type washing machines, the compositions perform satisfactorily, as would be expected from a knowledge of their components with respect to usual washing effect characteristics but additionally they significantly promote soil release from such materials. They are also satisfactory for washing nylons, cottons, acetates and blends of fibrous materials and promote soil release from such materials too, although not to the same great extent as with the polyesters. In tests of the washing and soil release actions of the compositions a Whirlpool Suds Saver washing machine was used, the water temperature was about 45°C and the water contained a total of about 200 p.p.m. hardness as $CaCO_3$, of mixed calcium and magnesium ions. The washing times were all about fifteen minutes and the laundry:water ratio was about 1:20, by weight. Items were rinsed twice automatically and then were dried in an automatic laundry dryer.

Soil release promotion is an important characteristic of the compositions of the present invention and of the disclosed washing method because it has long been known that oily soils, such as motor oils and greases, have an affinity for synthetic organic polymeric fibrous materials and are often difficult to remove from them with conventional washing preparations. Thus, the presence of the present soil release promoting polymer significantly aids in the removal of such oily soils or stains from the laundry and improves the products' detergencies. Such effect is more significant on repeated launderings, usually up to five launderings of the washed materials with the present compositions (or with equivalent wash water solutions). Yet, despite the apparent deposition of the soil release polymer on the substrate materials such materials do not become waxy.to the touch, do not change significantly in appearance or in normal desirable characteristics and do not block or inhibit the flow of moisture, so that evaporation of a wearer's perspiration is not prevented. Thereby the present compositions provide soil release without objectionable characteristics that otherwise might attend such release and they improve the comfort to the wearer of the washed garments. If anhydrous or essentially anhydrous polymer is employed, if the moisture content of the rest of the detergent composition is maintained low, not being greater than about 10% and preferably being held to 5% or less, if the product is not excessively alkaline, and if storage conditions are not excessively humid, the final compositions are of satisfactory stability during storage for reasonable periods, so that the polymers do not objectionably hydrolyze or otherwise decompose or transesterify, which could adversely affect their soil release and comfort characteristics. Even when more moisture and alkali are present useful products are obtainable but it may be desirable to utilize higher percentages of the soil release promoting polymer to allow for some detrimental effects of further decompositions on storage under adverse conditions.

In addition to users of the present products noting the improved soil release in washing normal loads of laundry containing articles soiled with oils or greases, comparative tests wherein dirty motor oil is applied to swatches of polyester and polyester-cotton blend materials and such swatches are washed in either the compositions of the present invention or control compositions, the same as those of the invention but without the soil release promoting polymer, also show improved soil release for the products of the present invention after repeated use. In such tests skilled observers note the

improvement in soil removal by the compositions of the present invention. Such results are further borne out by reflectometer checks of the washed materials, which also establish that the compositions of the present invention are of improved anti-redeposition capabilities when tested against oily and greasy soils.

When variations of the above formulas are made, changing the proportion of polymer plus or minus 20% and plus or minus 50% (to 1.5, 2.4, 3.6 and 4.5%), similar results are obtainable but with the greater proportions of polymer the soil release effects are better. Similarly, when such changes are made in the builder, nonionic detergent and the bentonite, polyacrylate and enzyme components, keeping the formulas within the ranges previously given, useful products result, of improved soil release, anti-redeposition and comfort characteristics.

When the highly preferred polyester soil release material is replaced by other such polyesters of molecular weights and/or ethylene terephthalate:polyoxyethylene terephthalate ratios and/or ethylene oxide:terephthalate moiety ratios, such as Alkaril Chemicals, Inc. HS-15, 2056-35, 2056-36, 3056-38, 3056-39 and 3056-40, which are of lower molecular weights and differing hydrophile:hydrophobe ratios, soil release properties of the detergent compositions are not as good, as a rule, and neither are anti-redeposition and "comfort" characteristics. Such is also usually the situation with polyesters wherein the polyoxyethylene unit weight is less than 3,000, e.g. 500 to 700, even at the prescribed molecular weight, but such materials can be used and may be of acceptable soil release promoting action under certain conditions and for particular materials and soils, if they are applied to the base builder beads as described.

Examples 5 to 8

The compositions of Examples 1—4 were made up without the soil release polymer being present. The polymer was added to the wash water concurrently or after the addition of the rest of the detergent composition, either as a liquid dispersion or in finely divided particulate form, and desirable washing and soil release results were obtainable. Thus, when a polyethylene terephthalate-polyoxyethylene terephthalate copolymer of a weight average molecular weight of about 22,000, with most of the polymer being of molecular weights in the range of 20,000 to 25,000, with the polyoxyethylene terephthalate component thereof being of a molecular weight of about 3,400, ranging from about 3,000 to 3,700 or 4,000, with the molar ratio of units of polyethylene terephthalate to units of polyoxyethylene terephthalate in the polymer being about 3:1 and with the molar ratio of ethylene oxide to phthalic moiety being about 22:1, and with the percentage of such polymer in the wash water being about 0.002%, essentially the same washing effect and accompanying soil release promoting, anti-redeposition and comfort characteristics are obtained whether the detergent composition containing the polymer is charged to the wash water or whether the detergent composition less polymer is first charged, followed by addition of the desired proportion of Alkaril QCF or Alkaril QCJ, in liquid dispersion (about 16% solids, in water) or as a particulate, preferably finely divided, solid. The washing conditions and tests employed were the same as those recited in Examples 1—4, above. Similarly (to Examples 1—4) when the less preferable soil release promoting polymers mentioned in Examples 1—4 are added to the wash water with or after the balance of the detergent composition components less satisfactory but useful results may be obtained.

Example 9

78.7 Parts by weight of the base beads described in Example 1 (which do not contain nonionic detergent, perfume, enzyme powder or soil release promoting polymer) were sprayed (or otherwise blended) with 19.4 parts of Alfonic 1214-60C nonionic detergent at an elevated temperature, as described for Examples 1—4. Alkaril QCF, (a solid form of the polymer, containing no surfactant dispersing agent and containing no more than 2% of moisture) was also mixed with the nonionic sprayed base beads to produce a detergent composition containing 2.9% of polymer. Clean swatches of various types were washed in a Whirlpool automatic washing machine of the top loading type, having a washing drum of 17 U.S. gallons (litres) capacity. After addition of the swatches in a standard wash load of about eight pounds (kgs), forty grams of the detergent composition, which had a bulk density of about 0.5 g/cc, were added to the wash water, which was of about 200 parts per million, as calcium carbonate, of mixed calcium and magnesium hardness, and which was at a temperature of about 49°C. Two swatches were employed of each of six different fabrics. The fabrics were washed, using a normal wash cycle for the washing machine, including rinsing, and subsequently the swatches were dried.

After drying the swatches were soiled in the centres thereof with equal volumes (about three drops) of used dirty motor oil and then they were rewashed with the same detergent composition. Whiteness readings of the stained areas of the swatches were taken, using a reflectometer. Because such readings represent whiteness and the used motor oil was black, the readings were directly proportional to effectiveness of the soil release promoting action of the detergent composition containing the polyethylene-polyoxyethylene copolymer. The same test was run for controls, in which the swatches were first washed in the detergent composition minus the polyethylene-polyoxyethylene polymer, subsequently, stained with the dirty motor oil, and then rewashed with the

same control composition. Also, whiteness readings were taken of the unsoiled swatches, for comparison. The results are given in Table 2 below.

Table 2

Swatch material	*Whiteness reading (Rd)*		
	Experimental	*Control*	*Unsoiled*
Single knit Dacron (Trade Mark)	89	37	89
Double knit Dacron	87	40	88
Dacron/cotton blend (65/35)	76	60	88
Terrycloth cotton (14% polyester content)	77	68	90
Percale cotton	78	76	90
Qiana (Trade Mark) nylon	56	57	88

As the data shows, and as is very readily visually verifiable, oil release is virtually 100% for the all-Dacron swatches and is significantly better than the control for Dacron/cotton and terrycloth cotton swatches. Little improvement is noticeable for percale cotton, and Qiana nylon does not appear to have had the release of the oily soil promoted by the preliminary washing thereof with the detergent composition containing the polyethylene-polyoxyethylene copolymer. However, it has been found that some nylons do have soil more readily removed from them after treatment with the detergent compositions of the foregoing examples and some cottons also show such results. Additionally, useful anti-redeposition effects on the various materials shown above are also verifiable by use of the reflectometer and similar tests wherein soil is added to the wash water and the amount thereof depositing on the swatches during discharge of the wash water from the washing machine is measured.

In addition to the described soil release promoting and anti-redeposition properties, the washed swatches also comparatively readily allow the transpiration of moisture vapour and promote evaporation of water on the surfaces thereof, unlikely normally waxy deposits on textiles, such as quaternary fabric softening chemicals and other hydrophobes.

Results like those given in this example are also obtainable by use of the compositions of Examples 1—8 and by separate additions of Alkaril QCF in particulate or aqueous dispersion form to the washing machine. Additionally, the compositions may be used in concentrated aqueous solution and/or suspension, e.g. 2 to 30% (or 5 to 10%), to pretreated, before washing, portions of clothing items that are likely to be soiled with oily materials. Such use is to prevent subsequent hard-to-remove soiling and is particularly appropriate for shirt collars and cuffs, work gloves and aprons, for example.

Many variations of the above formulas can be made, utilizing other nonionic detergents, other builders and builder combinations and other soil release promoting polymers within the present invention. Also, the various proportions may be changed within the ranges given, and useful effects of the desired types will result. It is surprising that the present compositions are so effective and of acceptable and practical stability because it has been found that builders, such as water soluble salts, have an adverse effect on polyethylene terephthalate-polyoxyethylene terephthalate copolymers in other built detergent compositions, apparently promoting hydrolysis and deterioration thereof which may make such materials unsatisfactory as soil release agents, and may also change the characteristics of the copolymers so that they make fabrics on which they are deposited uncomfortable to the wearer. Surprisingly, in the present compositions, although water soluble salts may be present, apparently due to the use of the nonionic detergent and possibly to some extent also due to the presence of insoluble builder, such as zeolite, in preferred compositions and the use of bentonite in some of these compositions, such interference of the builder salt is inhibited sufficiently so as to allow detergent compositions of useful stability to be made. Also good results may be attributed to the lesser proportions of the composition that are used in the wash water, so that the builder concentrations are lower and any undesirable effects thereof in the wash water are diminished. The nonionic-polymer combination is also important.

The particular preferred polymers, although high in content of hydrophile are also satisfactorily substantive to textiles washed with them, such as polyesters and polyester-cotton blends, and impart soil release and comfort properties to such fibrous materials. Thus, they have a satisfactory balance of properties, being sufficiently hydrophobic to be adherent to the substrates on which they are desired to be deposited, and at the same time not being excessively hydrophobic. They are hydrophilic enough to promote soil release and allow moisture transmission, and are not excessively soluble. Although it might be expected that a high hydrophile content of the product would make it susceptible to further hydrolysis and inactivation in the presence of moisture, such is not the case with the present compositions. Finally, the combination of nonionic detergent and soil release agent, with the aid of the above-mentioned builders, results in a product which is exceptionally effective in removing oily and greasy soils and stains from synthetic fabrics of the polyester and amide types, which stains are those considered by most experts to be among the most difficult to remove from laundry. Thus, the present

detergent compositions are significantly improved washday products and the washing processes represent advances in the art.

Example 10

Examples 1—4 were repeated but the detergent products were made from the spray dried base beads by spraying onto the tumbling bead surfaces a normally waxy nonionic detergent-polymer solution comprising 20 parts of the nonionic detergent and 3 parts of the polymer while the beads were being mixed in a tumbling drum or equivalent apparatus. The tumbling drum was inclined at about 7°, rotated at about 4—20 r.p.m. (depending on the state of spraying) and tumbling lasted for about 4 to 6 minutes. The solution sprayed was at a temperature of about 50°C, as were the tumbled base beads, the spraying was through a pressure nozzle which produced droplets in the 50 to 500 micron range, and the spray was directed onto a falling curtain of moving base beads. Instead of Alfonic 1214-60C, Neodol 23-6.5, 23-7, or 25-7, and sometimes 45-11 may be substituted, at least in part. The quantity of nonionic detergent-polymer solution sprayed was such as to result in the final products containing 20% of nonionic detergent and 3% of polymer as indicated in the formulas. The proteolytic enzyme was applied in powdered form to result in the desired concentration in the product, and perfume was sprayed onto the product to the extent of its desired concentration therein. The resulting detergent compositions were of bulk densities about the same as or up to 0.1 g/ml higher than those of the base beads, but were within the ranges previously recited. The products were attractive and regular in appearance, and were free flowing and non-dusting.

The detergent compositions described above are excellent heavy duty laundry detergents and are especially useful for washing household laundry in automatic washing machines. When employed at a concentration of about 0.05 to 0.15%, e.g. 0.06% in a top loading 17 gallon (U.S.) (litres) capacity washer, in the washing of normal loads of 100% polyester and 65% polyester-35% cotton fabrics in home laundry or commercial washing machines, whether of the top loading or front loading types, or at higher concentrations in European type washing machines, the compositions perform satisfactorily in the manner described and the polymer exerts improved soil release actions after storage, compared to the polymer in "unprotected" compositions wherein hydrolysis or other degradation of the polymer can occur more readily.

When the highly preferred polyester soil release material is replaced by other such polyesters of molecular weights and/or ethylene terephthalate:polyoxyethylene terephthalate unit ratios and/or ethylene oxide:terephthalate moiety ratios, such as Alkaril Chemicals, Inc. HS-15, 2056-35, 2056-36, 2056-38, 2056-39 and 2056-40, which are of lower molecular weights and differing hydrophile:hydrophobe ratios, acceptable solutions of polymer in detergent are made but the soil release properties of the detergent compositions are not as good, as a rule, and neither are anti-redeposition and "comfort" characteristics. Such is also usually the situation with polyesters wherein the polyoxyethylene unit weight is less than 3,000, e.g. 500 to 700, even at the prescribed molecular weight, but such materials can be used and may be of acceptable soil release promoting action under certain conditions and for particular materials and soils. Changes in the nonionic detergent to others previously mentioned do not seem to have detrimental effects on soil release properties of the product. The reported good results are also obtainable when the proportion of polymer in the spray and in the final product is changed, as in Examples 1—4.

Example 11

78.7 Parts by weight of the base beads described in Example 1 (which do not contain nonionic detergent, perfume, enzyme powder or soil release promoting polymer) at a temperature of about 50°C were sprayed with a standard sprayer (or were otherwise blended) with 19.4 parts of Alfonic 1214-60C nonionic detergent and 2.9 parts of Alkaril QCF, (a solid form of the polymer, containing no surfactant dispersing agent and containing no more than 2% of moisture) dissolved in the detergent, which was also at a temperature of about 50°C. The spraying was of continuously moving surfaces of the beads as they were tumbled in an inclined tumbling drum. The products made were tested, as described in Example 9, and the results were satisfactory, even after storage of the product.

Claims

1. A particulate built nonionic synthetic organic detergent composition which comprises from 5 to 30% of synthetic organic nonionic detergent, 30 to 80% of builder for such detergent, 1 to 20% of water, and a percentage, within the range of 0.5 to 20% of a soil release promoting polymer of polyethylene terephthalate and polyoxyethylene terephthalate.

2. A particulate built nonionic synthetic organic detergent composition which comprises from 5 to 30% of synthetic organic nonionic detergent, 30 to 80% of builder for such detergent, 1 to 20% of water, and a percentage, within the range of 0.5 to 20% of a soil release promoting polymer of polyethylene terephthalate and polyoxyethylene terephthalate, in which detergent composition the nonionic detergent is absorbed into absorbent particles of the builder and the soil release promoting polymer is also post-applied to the said particles.

3. A detergent composition as claimed in Claim 1 or Claim 2 which has a bulk density in the range 0.2 to 0.9 g/cc.

4. A detergent composition as claimed in Claim 3 which has a bulk density in the range 0.4 to 0.9 g/cc.

5. A detergent composition as claimed in Claim 4 which has a bulk density in the range 0.6 to 0.9 g/cc.

6. A detergent composition as claimed in Claim 4 which has a bulk density in the range 0.4 to 0.7 g/cc.

7. A detergent composition as claimed in any one of Claims 1 to 6 which has particle sizes in the range No. 10 to 100 U.S. Sieve Series which have openings 2000 microns and 149 microns across respectively.

8. A detergent composition as claimed in any one of Claims 1 to 7 in which the nonionic synthetic organic detergent is a condensation product of a lower alkylene oxide and a higher fatty alcohol.

9. A detergent composition as claimed in Claim 8 in which lower alkylene oxide is ethylene oxide and the higher fatty alcohol is of 10 to 20 carbon atoms.

10. A detergent composition as claimed in Claim 9 in which the nonionic detergent is a condensation product of a higher fatty alcohol of 12 to 16 carbon atoms with 3 to 20 mols of ethylene oxide per mol of higher fatty alcohol.

11. A detergent composition as claimed in any one of Claims 1 to 10 in which the percentage of nonionic detergent in the composition is in the range 10 to 25%.

12. A detergent composition as claimed in any one of Claims 1 to 11 in which the builder is a water soluble or water insoluble builder or mixture thereof.

13. A detergent composition as claimed in Claim 12 in which the builder is a water softening zeolite, sodium carbonate, sodium bicarbonate, sodium tripolyphosphate, sodium pyrophosphate, sodium nitrilotriacetate or sodium silicate, or a mixture thereof.

14. A detergent composition as claimed in Claim 13 in which the builder is a mixture of sodium carbonate, sodium bicarbonate and hydrated crystalline sodium aluminosilicate, with the percentages thereof, on a detergent composition basis, being from 5 to 15%, 15 to 30% and 20 to 35%, respectively.

15. A detergent composition as claimed in Claim 13 in which the builder is a mixture of sodium carbonate, sodium bicarbonate and sodium silicate of $Na_2O:SiO_2$ ratio in the range of 1:2 to 1:2.4, with the percentages of builders, on a detergent composition basis, being from 15 to 35%, 20 to 40% and 2 to 15%, respectively.

16. A detergent composition as claimed in Claim 13 in which the builder is a mixture of hydrated crystalline sodium aluminosilicate, sodium nitrilotriacetate, sodium silicate and sodium carbonate, with the percentages thereof, on a detergent composition basis, being from 20 to 35%, 15 to 40%, 2 to 10% and 1 to 10%, respectively.

17. A detergent composition as claimed in Claim 13 in which the builder is a mixture of sodium polyphosphate and sodium silicate, with the percentages thereof, on a composition basis, being from 40 to 75% and 5 to 15%, respectively.

18. A detergent composition as claimed in any one of Claims 1 to 17 in which the percentage of water is 2 to 15%.

19. A detergent composition as claimed in Claim 18 in which the percentage of water is 4 to 12%.

20. A detergent composition as claimed in Claim 18 in which the percentage of water is 2 to 10%.

21. A detergent composition as claimed in any one of Claims 1 to 20 in which the percentage of soil release promoting polymer is 1 to 10%.

22. A detergent composition as claimed in Claim 21 in which the percentage of soil releasing polymer is 2 to 5%.

23. A detergent composition as claimed in any one of Claims 1 to 22 in which the soil release promoting polymer is of a molecular weight in the range 8000 to 60,000.

24. A detergent composition as claimed in Claim 23 in which the soil release promoting polymer has a molecular weight in the range of about 15,000 to 50,000.

25. A detergent composition as claimed in any one of Claims 1 to 24 in which the soil release promoting polymer is of a molecular weight in the range of about 19,000 to 43,000.

26. A detergent composition as claimed in Claim 25 in which the soil release promoting polymer is of a molecular weight in the range of about 19,000 to 25,000.

27. A detergent composition as claimed in Claim 26 in which the soil release promoting polymer is of a weight average molecular weight of about 22,000.

28. A detergent composition as claimed in any one of Claims 1 to 27 in which the polyoxyethylene of the polyoxyethylene terephthalate is of a molecular weight in the range of about 500 to 10,000.

29. A detergent composition as claimed in Claim 28 in which the polyoxyethylene of the polyoxyethylene terephthalate is of a molecular weight in the range of about 2,500 to 5,000.

30. A detergent composition as claimed in Claim 29 in which the polyoxyethylene of the polyoxyethylene terephthalate is of a molecular weight in the range of 3,000 to 4,000.

31. A detergent composition as claimed in Claim 30 in which the polyoxyethylene of the polyoxyethylene terephthalate is of a molecular weight of about 3,400.

32. A detergent composition as claimed in any one of Claims 1 to 31 in which in the soil release promoting polymer the molar ratio of ethylene terephthalate to polyoxyethylene terephthalate units is within the range of 2:1 to 6:1.

33. A detergent composition as claimed in Claim 32 in which the molar ratio of ethylene terephthalate to polyoxyethylene terephthalate units is within the range of 5:2 to 5:1.

34. A detergent composition as claimed in Claim 33 in which the molar ratio of ethylene terephthalate to polyoxyethylene terephthalate units in the polymer is within the range of 3:1 to 4:1.

35. A detergent composition as claimed in Claim 34 in which the molar ratio of ethylene terephthalate to polyoxyethylene terephthalate units in the polymer is about 3:1.

36. A detergent composition as claimed in any one of Claims 1 to 35 in which in the soil release promoting polymer the molar ratio of ethylene oxide to phthalic moiety is at least 10:1.

37. A detergent composition as claimed in Claim 36 in which the ratio is at least 15:1.

38. A detergent composition as claimed in Claim 37 in which the ratio is at least 20:1.

39. A detergent composition as claimed in Claim 38 in which the ratio is from 20:1 to 30:1.

40. A detergent composition as claimed in Claim 39 in which the ratio is about 22:1.

41. A detergent composition as claimed in Claim 1 having a bulk density in the range of 0.2 to 0.9 g/cc and particle sizes in the range of No. 10 to 100, U.S. Sieve Series which have openings 2000 microns and 149 microns across respectively, wherein the nonionic synthetic organic detergent is a condensation product of a lower alkylene oxide and a higher fatty alcohol, the percentage of such nonionic detergent in the composition is in the range from 10 to 25%, the builder is a water soluble or water insoluble builder or mixture thereof, the percentage of water is 2 to 15%, the percentage of soil release promoting, vapour transmitting polymer is from 1 to 10%, such polymer is of a molecular weight in the range of about 19,000 to 43,000, the polyoxyethylene of the polyoxyethylene terephthalate thereof is of a molecular weight in the range of about 2,500 to 5,000, the molar ratio of ethylene terephthalate to polyoxyethylene terephthalate units thereof is within the range of 5:2 to 5:1, and the molar ratio of ethylene oxide to phthalic moiety therein is at least 20:1.

42. A detergent composition as claimed in Claim 41 having a bulk density in the range of 0.4 to 0.9 g/cc wherein the nonionic synthetic organic detergent is a condensation product of ethylene oxide and a higher fatty alcohol of 10 to 20 carbon atoms, the builder is a water softening zeolite, sodium carbonate, sodium bicarbonate, sodium tripolyphosphate, sodium pyrophosphate, sodium nitrilotriacetate or sodium silicate, or a mixture thereof, the percentage of soil release promoting polymer present is in the range of 2 to 5%, the polymer is of a molecular weight in the range of about 19,000 to 25,000, the polyoxyethylene of the polyoxyethylene terephthalate is of a molecular weight in the range of 3,000 to 4,000, the molar ratio of ethylene terephthalate to polyoxyethylene terephthalate units in the polymer is within the range of 3:1 to 4:1, and the molar ratio of ethylene oxide to phthalic moiety therein is from 20:1 to 30:1.

43. A detergent composition as claimed in Claim 42 having a bulk density in the range of 0.6 to 0.9 g/cc wherein the nonionic detergent is a condensation product of a higher fatty alcohol of 12 to 16 carbon atoms with 3 to 20 mols of ethylene oxide per mol of higher fatty alcohol, the moisture content is in the range of 4 to 12%, the builder is a mixture of sodium carbonate, sodium bicarbonate and hydrated crystalline sodium aluminosilicate, with the percentages thereof, on a detergent composition basis, being from 5 to 15%, 15 to 30% and 20 to 35%, respectively, and the soil release promoting polymer is of a weight average molecular weight of about 22,000, the polyoxyethylene of the polyoxyethylene terephthalate is of a molecular weight of about 3,400, the molar ratio of ethylene terephthalate to polyoxyethylene terephthalate units in the polymer is about 3:1, and the molar ratio of ethylene oxide to phthalic moiety therein is about 22:1.

44. A detergent composition as claimed in Claim 42 having a bulk density in the range of 0.6 to 0.9 g/cc wherein the nonionic detergent is a condensation product of a higher fatty alcohol of 12 to 16 carbon atoms with 3 to 20 mols of ethylene oxide per mol of higher fatty alcohol, the moisture content is in the range of 2 to 10%, the builder is a mixture of sodium carbonate, sodium bicarbonate and sodium silicate of $Na_2O:SiO_2$ ratio in the range of 1:2 to 1:2.4, with the percentages of builders, on a detergent composition basis, being from 15 to 35%, 20 to 40% and 3 to 15%, respectively, the polymer is of a molecular weight of about 22,000, the polyoxyethylene of the polyoxyethylene terephthalate is of a molecular weight of about 3,400, the molar ratio of ethylene terephthalate to polyoxyethylene terephthalate units in the polymer is about 3:1, and the molar ratio of ethylene oxide to phthalic moiety therein is about 22:1.

45. A detergent composition as claimed in Claim 42, having a bulk density in the range of 0.6 to 0.9 g/cc wherein the nonionic detergent is a condensation product of a higher fatty alcohol of 12 to 16 carbon atoms with 3 to 20 mols of ethylene oxide per mol of higher fatty alcohol, the moisture content is in the range of 4 to 12%, the builder is a mixture of hydrated crystalline sodium aluminosilicate, sodium nitrilotriacetate, sodium silicate and sodium carbonate, with the percentages thereof, on a

composition basis, being from 20 to 35%, 15 to 40%, 2 to 10% and 1 to 10%, respectively, the soil release promoting polymer is of a molecular weight of about 22,000, the polyoxyethylene of the polyoxyethylene terephthalate is of a molecular weight of about 3,400, the molar ratio of ethylene terephthalate to polyoxyethylene terephthalate units in the polymer is about 3:1, and the molar ratio of ethylene oxide to phthalic moiety therein is about 22:1.

46. A detergent composition as claimed in Claim 42 having a bulk density in the range of 0.4 to 0.7 g/cc wherein the nonionic detergent is a condensation product of a higher fatty alcohol of 12 to 16 carbon atoms with 3 to 20 mols of ethylene oxide per mol of higher fatty alcohol, the moisture content is in the range of 4 to 12%, the builder is a mixture of sodium polyphosphate and sodium silicate, with the percentages thereof, on a composition basis, being from 40 to 75% and 5 to 15%, respectively, the polymer is of a molecular weight of about 22,000, the polyoxyethylene of the polyoxyethylene terephthalate is of a molecular weight of about 3,400, the molar ratio of ethylene terephthalate to polyoxyethylene terephthalate units in the polymer is about 3:1, and the molar ratio of ethylene oxide to phthalic moiety therein is about 22:1.

47. A detergent composition as claimed in any one of Claims 1 to 46 suitable for washing polyester fibrous materials and imparting soil release properties thereto, the percentage of the said polymer being sufficient to impart soil release properties to the said polyester fibrous materials washed with the detergent composition while maintaining them comfortable to a wearer and not preventing vapour transmission through them.

48. A detergent composition as claimed in Claim 2 having a bulk density in the range of 0.2 to 0.9 g/cc and particle sizes in the range of No. 10 to 100, U.S. Sieve Series which have openings 2000 microns across and 149 microns across respectively, wherein the nonionic synthetic organic detergent is a condensation product of a lower alkylene oxide and a higher fatty alcohol, the percentage of such nonionic detergent in the composition is in the range from 10 to 25%, the builder is a water soluble or water insoluble builder or mixture thereof, the percentage of water is 2 to 15%, the percentage of soil release promoting polymer is from 1 to 10%, such polymer is of a weight average molecular weight in the range of about 15,000 to about 50,000, and a melting point in the range of 45 to 65°C, the polyoxyethylene of the polyoxyethylene terephthalate thereof is of a molecular weight in the range of about 500 to 10,000, the molar ratio of ethylene terephthalate to polyoxyethylene terephthalate units thereof is within the range of 2:1 to 6:1, and the molar ratio of ethylene oxide to phthalic moiety therein is at least 10:1.

49. A detergent composition as claimed in Claim 48 having a bulk density in the range of 0.4 to 0.9 g/cc wherein the nonionic synthetic organic detergent is a condensation product of ethylene oxide and a higher fatty alcohol of 10 to 20 carbon atoms, the builder is a water softening zeolite, sodium carbonate, sodium bicarbonate, sodium tripolyphosphate, sodium pyrophosphate, sodium nitrilotriacetate or sodium silicate, or a mixture thereof, the percentage of soil release promoting polymer present is in the range of 2 to 5%, the polymer is of a weight average molecular weight in the range of about 15,000 to 50,000, the polyoxyethylene of the polyoxyethylene terephthalate is of a molecular weight in the range range of 2,500 to 5,000, the molar ratio of ethylene terephthalate to polyoxyethylene terephthalate units in the polymer is within the range of 5:2 to 5:1, and the molar ratio of ethylene oxide to phthalic moiety therein is at least 15:1.

50. A detergent composition as claimed in Claim 1 substantially as specifically described herein with reference to any of the Examples 1 to 4, 9, 10 or 11.

51. A detergent composition as claimed in Claim 2 substantially as specifically described herein with reference to Examples 1 to 4, 9, 10 and 11.

52. A method of washing synthetic organic polymeric fibrous materials and simultaneously imparting soil release properties to them while maintaining them comfortable to a wearer and not preventing vapour transmission through them, when the materials are dried, which comprises washing such a synthetic material in an aqueous medium in a washing machine tub, which medium contains from 0.005 to 0.15% of synthetic organic nonionic detergent, 0.03 to 0.40% of builder for such detergent, and a percentage, within the range of 0.0005 to 0.10%, sufficient to impart soil release properties to the synthetic organic polymeric fibrous materials being washed, while maintaining them comfortable to a wearer and not preventing vapour transmission through them, when dried, of a soil release promoting polymer of polyethylene terephthalate and polyoxyethylene terephthalate.

53. A detergent composition as claimed in Claim 52 in which the soil release promoting polymer is of a molecular weight in the range 8000 to 60,000.

54. A detergent composition as claimed in Claim 53 in which the soil release promoting polymer has a molecular weight in the range of about 15,000 to 50,000.

55. A detergent composition as claimed in Claim 54 in which the soil release promoting polymer is of a molecular weight in the range of about 19,000 to 43,000.

56. A detergent composition as claimed in Claim 55 in which the soil release promoting polymer is of a molecular weight in the range of about 19,000 to 25,000.

57. A detergent composition as claimed in Claim 56 in which the soil release promoting polymer is of a weight average molecular weight of about 22,000.

58. A detergent composition as claimed in any one of Claims 52 to 57 in which the polyoxyethylene of the polyoxyethylene terephthalate is of a molecular weight in the range of about 500 to 10,000.

59. A detergent composition as claimed in Claim 58 in which the polyoxyethylene of the polyoxyethylene terephthalate is of a molecular weight in the range of about 2,500 to 5,000.

60. A detergent composition as claimed in Claim 59 in which the polyoxyethylene of the polyoxyethylene terephthalate is of a molecular weight in the range of 3,000 to 4,000.

61. A detergent composition as claimed in Claim 60 in which the polyoxyethylene of the polyoxyethylene terephthalate is of a molecular weight of about 3,400.

62. A detergent composition as claimed in any one of Claims 52 to 61 in which in the soil release promoting polymer the molar ratio of ethylene teerphthalate to polyoxyethylene terephthalate units is within the range of 2:1 to 6:1.

63. A detergent composition as claimed in Claim 62 in which the molar ratio of ethylene terephthalate to polyoxyethylene terephthalate units is within the range of 5:2 to 5:1.

64. A detergent composition as claimed in Claim 63 in which the molar ratio of ethylene terephthalate to polyoxyethylene terephthalate units in the polymer is within the range of 3:1 to 4:1.

65. A detergent composition as claimed in Claim 64 in which the molar ratio of ethylene terephthalate to polyoxyethylene terephthalate units in the polymer is about 3:1.

66. A detergent composition as claimed in any one of Claims 52 to 65 in which in the soil release promoting polymer the molar ratio of ethylene oxide to phthalic moiety is at least 10:1.

67. A detergent composition as claimed in Claim 66 in which the ratio is at least 15:1.

68. A detergent composition as claimed in Claim 67 in which the ratio is at least 20:1.

69. A detergent composition as claimed in Claim 68 in which the ratio is from 20:1 to 30:1.

70. A detergent composition as claimed in Claim 69 in which the ratio is about 22:1.

71. A method as claimed in Claim 52 substantially as specifically described herein with reference to Examples 5 to 8.

72. A process for the manufacture of a soil release promoting particulate built nonionic synthetic organic detergent composition which comprises preparing particles of a builder or a mixture of builders for a nonionic detergent, dissolving and/or dispersing in such nonionic detergent in liquid state a substantially anhydrous soil release promoting polymer of polyethylene terephthalate and polyoxyethylene terephthalate and spraying such liquid nonionic detergent-polymer mixture onto moving surfaces of the builder particles to distribute such nonionic detergent and polymer over such particles.

73. A detergent composition as claimed in Claim 72 in which the soil release promoting polymer is of a molecular weight in the range 8000 to 60,000.

74. A detergent composition as claimed in Claim 73 in which the soil release promoting polymer has a molecular weight in the range of about 15,000 to 50,000.

75. A detergent composition as claimed in Claim 74 in which the soil release promoting polymer is of a molecular weight in the range of about 19,000 to 43,000.

76. A detergent composition as claimed in Claim 75 in which the soil release promoting polymer is of a molecular weight in the range of about 19,000 to 25,000.

77. A detergent composition as claimed in Claim 76 in which the soil release promoting polymer is of a weight average molecular weight of about 22,000.

78. A detergent composition as claimed in any one of claims 72 to 77 in which the polyoxyethylene of the polyoxyethylene terephthalate is of a molecular weight in the range of about 500 to 10,000.

79. A detergent composition as claimed in Claim 78 in which the polyoxyethylene of the polyoxyethylene terephthalate is of a molecular weight in the range of about 2,500 to 5,000.

80. A detergent composition as claimed in Claim 79 in which the polyoxyethylene of the polyoxyethylene terephthalate is of a molecular weight in the range of 3,000 to 4,000.

81. A detergent composition as claimed in Claim 80 in which the polyoxyethylene of the polyoxyethylene terephthalate is of a molecular weight of about 3,400.

82. A detergent composition as claimed in any one of Claims 72 to 81 in which in the soil release promoting polymer the molar ratio of ethylene terephthalate to polyoxyethylene terephthalate units is within the range of 2:1 to 6:1.

83. A detergent composition as claimed in Claim 82 in which the molar ratio of ethylene terephthalate to polyoxyethylene terephthalate units is within the range of 5:2 to 5:1.

84. A detergent composition as claimed in Claim 83 in which the molar ratio of ethylene terephthalate to polyoxyethylene terephthalate units in the polymer is within the range of 3:1 to 4:1.

85. A detergent composition as claimed in Claim 84 in which the molar ratio of ethylene terephthalate to polyoxyethylene terephthalate units in the polymer is about 3:1.

86. A detergent composition as claimed in any one of Claims 82 to 85 in which in the soil release promoting polymer the molar ratio of ethylene oxide to phthalic moiety is at least 10:1.

87. A detergent composition as claimed in Claim 86 in which the ratio is at least 15:1.

88. A detergent composition as claimed in Claim 87 in which the ratio is at least 20:1.

89. A detergent composition as claimed in Claim 88 in which the ratio is from 20:1 to 30:1.

90. A detergent composition as claimed in Claim 89 in which the ratio is about 22:1.

91. A process as claimed in any one of Claims 72 to 90 wherein the builder particles are made by crutching the builder or mixture of builders in an aqueous medium and spray drying such mix at an elevated temperature.

92. A process as claimed in any one of Claims 72 to 91 in which the nonionic detergent is heated to a temperature in the range of 40 to 70°C, at which it is liquid, and the polymer is dissolved in the heated nonionic detergent.

93. A process as claimed in Claim 92 in which the solution of polymer in nonionic detergent is sprayed onto moving surfaces of the builder particles while such particles are being tumbled in tumbling apparatus to present new surfaces to the nonionic detergent-polymer solution spray.

94. A process as claimed in any one of Claims 72 to 93 in which the soil release promoting polymer is of a moisture content less than 5%.

95. A process as claimed in Claim 72, wherein the builder particles are made by crutching the builder or mixture of builders in an aqueous medium and spray drying such mix at an elevated temperature to particles of sizes in the range of No. 10 to 100, U.S. Sieve Series which have openings of 2000 microns and 149 microns respectively, and of a bulk density in the range of 0.2 to 0.9 g/cc, the nonionic synthetic organic detergent is a condensation product of a lower alkylene oxide and a higher fatty alcohol, the polymer is of a molecular weight in the range of 19,000 to 43,000, the polyoxyethylene of the polyoxyethylene terephthalate thereof is of a molecular weight in the range of about 2,500 to 5,000, the molar ratio of ethylene terephthalate to polyoxyethylene terephthalate units in the polymer is within the range of 5:2 to 5:1, and the molar ratio of ethylene oxide to phthalic moiety therein is at least 15:1, the nonionic detergent is heated to a temperature in the range of 40 to 70°C, at which it is liquid, the polymer is of a moisture content less than 5%, the polymer is dissolved in the heated nonionic detergent and the solution of a polymer in such detergent is sprayed onto moving surfaces of the builder particles while such particles are being tumbled in tumbling apparatus to present new surfaces to the nonionic detergent-polymer solution spray.

96. A process as claimed in any one of Claims 92 to 95, wherein the nonionic detergent is normally solid, the proportion of polymer dissolved in the nonionic detergent is from 5 to 30% of the resulting solution, and the temperature of such solution, when it is sprayed onto the tumbling builder particles, is within the range of 45 to 55°C.

97. A process as claimed in Claim 96 in which the crutcher mix and the spray dried beads contain moisture and adjuvant(s), the proportion of builder in the spray dried beads is from 60 to 99%, the moisture content of such beads is from 1 to 20%, the builder is a water softening zeolite, sodium carbonate, sodium bicarbonate, sodium tripolyphosphate, sodium pyrophosphate, sodium nitrilotriacetate or sodium silicate, or a mixture thereof, and the proportion of nonionic detergent-polymer solution sprayed onto the spray dried builder beads is such that the detergent composition made thereby comprises from 5 to 30% of nonionic synthetic organic detergent, 30 to 80% of a builder or mixture of builders for such detergent, 1 to 20% of water and a percentage, within the range of 0.5 to 20%, sufficient to impart soil release properties to synthetic organic polymeric fibrous materials washed with the detergent composition while maintaining them comfortable to a wearer and permitting vapour transmission through them, of the polymer of ethylene terephthalate and polyoxyethylene terephthalate.

98. A process as claimed in Claim 97, wherein the proportion of polymer dissolved in the nonionic detergent is from 5 to 20% of the resulting solution and about 15 to 30 parts thereof are sprayed onto 85 to 70 parts of spray dried builder beads to make a detergent composition containing 10 to 25% of nonionic detergent, 30 to 80% of a builder or mixture of builders, 2 to 15% of moisture and 1 to 10% of the polymer.

99. A process as claimed in Claim 72 substantially as specifically described herein with reference to Examples 1 to 4, 9, 10 or 11.

100. A liquid composition, suitable for spraying onto detergent builder particles to produce a soil release promoting particulate built nonionic synthetic organic detergent composition, which comprises nonionic detergent and soil release promoting polymer of polyethylene terephthalate and polyoxyethylene terephthalate.

101. A composition as claimed in Claim 100, wherein the nonionic detergent is a normally solid condensation product of higher fatty alcohol and ethylene oxide or ethylene glycol, the polymer is of a molecular weight in the range of about 8,000 to 60,000 and the polymer is dissolved in the nonionic detergent.

102. A composition as claimed in Claim 100 or Claim 101 in which the moisture content of the composition is no greater than 5%.

103. A composition as claimed in any one of Claims 100 to 102 in which the nonionic synthetic organic detergent is a condensation product of a lower alkylene oxide and a higher fatty alcohol.

104. A composition as claimed in Claim 103 in which lower alkylene oxide is ethylene oxide and the higher fatty alcohol is of 10 to 20 carbon atoms.

105. A composition as claimed in Claim 104 in which the nonionic detergent is a condensation product of a higher fatty alcohol of 12 to 16 carbon atoms with 3 to 20 mols of ethylene oxide per mol of higher fatty alcohol.

106. A composition as claimed in any one of Claims 100 to 105 in which the soil release promoting polymer is of a molecular weight in the range 8000 to 60,000.

107. A composition as claimed in Claim 106 in which the soil release promoting polymer has a molecular weight in the range of about 15,000 to 50,000.

108. A detergent composition as claimed in any one of Claims 100 to 107 in which the soil release promoting polymer is of a molecular weight in the range of about 19,000 to 43,000.

109. A detergent composition as claimed in Claim 108 in which the soil release promoting polymer is of a molecular weight in the range of about 19,000 to 25,000.

110. A detergent composition as claimed in Claim 109 in which the soil release promoting polymer is of a weight average molecular weight of about 22,000.

111. A detergent composition as claimed in any one of Claims 100 to 110 in which the polyoxyethylene of the polyoxyethylene terephthalate is of a molecular weight in the range of about 500 to 10,000.

112. A detergent composition as claimed in Claim 111 in which the polyoxyethylene of the polyoxyethylene terephthalate is of a molecular weight in the range of about 2,500 to 5,000.

113. A detergent composition as claimed in Claim 112 in which the polyoxyethylene of the polyoxyethylene terephthalate is of a molecular weight in the range of 3,000 to 4,000.

114. A detergent composition as claimed in Claim 113 in which the polyoxyethylene of the polyoxyethylene terephthalate is of a molecular weight of about 3,400.

115. A detergent composition as claimed in any one of Claims 100 to 114 in which in the soil release promoting polymer the molar ratio of ethylene terephthalate to polyoxyethylene terephthalate units is within the range of 2:1 to 6:1.

116. A detergent composition as claimed in Claim 115 in which the molar ratio of ethylene terephthalate to polyoxyethylene terephthalate units is within the range of 5:2 to 5:1.

117. A detergent composition as claimed in Claim 116 in which the molar ratio of ethylene terephthalate to polyoxyethylene terephthalate units in the polymer is within the range of 3:1 to 4:1.

118. A detergent composition as claimed in Claim 117 in which the molar ratio of ethylene terephthalate to polyoxyethylene terephthalate units in the polymer is about 3:1.

119. A detergent composition as claimed in Claim 118 in which in the soil release promoting polymer the molar ratio of ethylene oxide to phthalic moiety is at least 10:1.

120. A detergent composition as claimed in Claim 119 in which the ratio is at least 15:1.

121. A detergent composition as claimed in Claim 120 in which the ratio is at least 20:1.

122. A detergent composition as claimed in Claim 121 in which the ratio is from 20:1 to 30:1.

123. A detergent composition as claimed in Claim 122 in which the ratio is about 22:1.

124. A composition as claimed in Claim 100 to 123, wherein the nonionic detergent is a condensation product of a higher fatty alcohol of 12 to 16 carbon atoms with 3 to 20 mols of ethylene oxide per mol of higher fatty alcohol, the polymer is of a molecular weight in the range of about 15,000 to 50,000, the polyoxyethylene of the polyoxyethylene terephthalate is of a molecular weight in the range of about 1,000 to 10,000, the molar ratio of ethylene terephthalate to polyoxyethylene terephthalate units thereof is within the range of 2:1 to 6:1, the composition is essentially anhydrous with a moisture content less than 0.5%, the composition is at a temperature in the range of 40 to 70°C and the concentration of polymer in the composition is within the range of 5 to 30%.

125. A composition as claimed in Claim 100 substantially as specifically described herein with reference to Examples 1 to 4, 10 or 11.

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